

The infrared and Raman spectra of propranolol hydrochloride

J Marshall

Department of Physics, Loyola College, Madras-600 034, India
and

S Gunasekaran

Department of Physics, Pachaiyappa's College, Madras-600 030, India

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Abstract : The propranolol hydrochloride molecule comprises of two parts : one part being substituted naphthalene while the other is an aliphatic chain of 2 propanol-1-1-(1-methyl ethyl amino) group. The assignment of the observed frequencies for the molecule is based on this partitioned structure. The molecule has C_s point group of symmetry.

Keywords : Infrared and Raman spectra, propranolol hydrochloride molecule assignment

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1. Introduction

Blood pressure is the pressure exerted on the walls of the vessels by the circulating blood and this depends upon the activity of the vasoconstrictor and vasodilator nerves and several other factors. The two main factors are the cardiac output and peripheral resistance. The cardiac output is responsible for the systolic pressure while the peripheral resistance is reflected in the diastolic pressure. Both the cardiac output and the peripheral resistance are under the control of the nervous system, chiefly the vagus and vasomotor centres so that the brain can always adjust the blood pressure as may be necessary. These two centres are regulated by reflexes from Carotid sinus and Aortic arch. They are also influenced by drugs called the antihypertensives which act through the autonomic nervous system (peripherally). The antihypertensives come under two categories, the Ganglion blockers and the Receptor blockers commonly called Beta blockers like propranolol. These drugs cause vasodilation and are used in the treatment of hypertension. Propranolol is one of the recent drugs which is currently receiving a lot of attention in the treatment and management of essential

hypertension. The structure of propranolol hydrochloride is given in Figure 1. The vibrations of the molecule can be viewed as separately comprising of a substituted

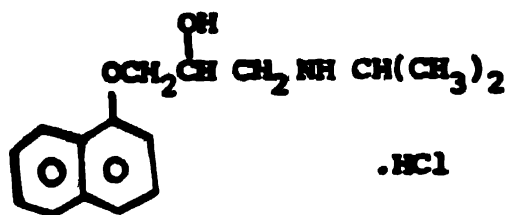


Figure 1. Structure of propranolol hydrochloride.

naphthalene group and a chain aliphatic structure of 2 propanol-1-(1-methyl ethyl amino) group.

2. Experimental

The infrared spectrum was recorded on a Perkin Elmer 640 spectrometer in the range $4000 - 625 \text{ cm}^{-1}$ is presented in Figure 2. The Raman spectrum was recorded on a

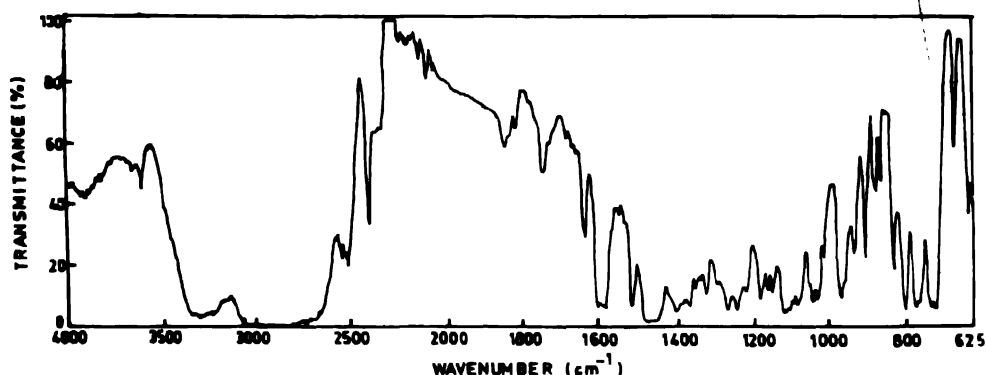


Figure 2. IR spectrum of propranolol hydrochloride.

DILOR Z 24 spectrometer in the range $4000 - 10 \text{ cm}^{-1}$ is presented in Figure 3. The sampling technique was KBr pellet in both cases. The probable assignments for the molecule is given in Table 1.

3. Result and discussion

3.1. Skeleton vibrations :

The assignment of various modes of vibration for the mono-substituted naphthalene part of the molecule is based on the previous works undertaken in this field [1-8]. The C-C ring stretching vibration occurs in the range $1266 - 1615 \text{ cm}^{-1}$. The C-C ring stretches for the naphthalene molecule are the b_{3g} (1624 cm^{-1}), b_{1u} (1601 cm^{-1}), a_g (1579 cm^{-1}), b_{2u} (1508 cm^{-1}), the b_{1u} (1268 cm^{-1}). All of these modes have been identified for the present molecule

to occur at 1630, 1590, 1532, 1512 and 1270 cm^{-1} in the infrared spectrum while the a_g (1579 cm^{-1}) mode is found to occur at 1583 cm^{-1} in the Raman spectrum. All C-C ring stretching vibrations belong to a' species in C_s symmetry. In naphthalene the out-of-plane skeletal deformations are the b_{3u} (780 cm^{-1}) and the a_u (740 cm^{-1}) modes. The frequencies

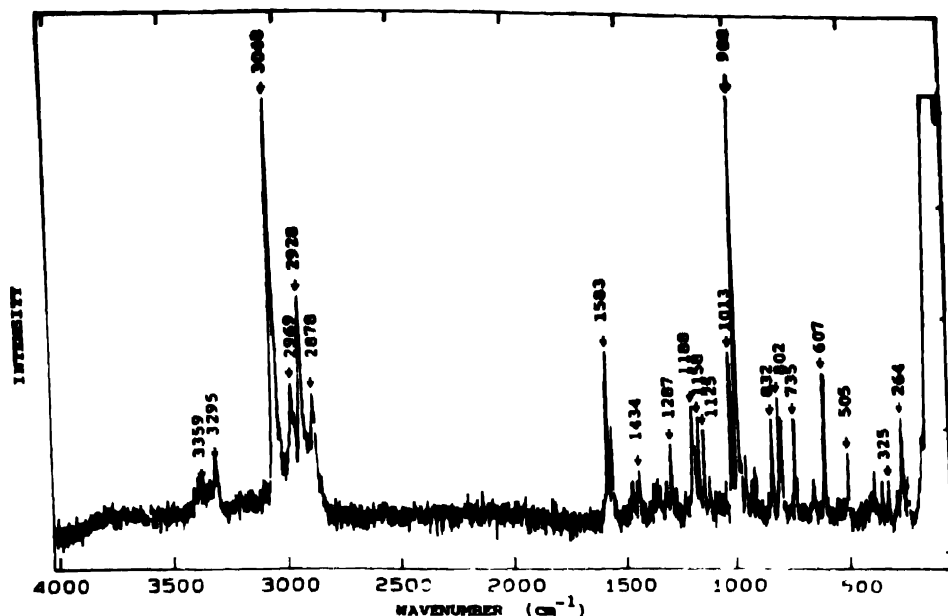


Figure 3. Raman spectrum of propranolol hydrochloride.

at 775 cm^{-1} and the doublet at about 732 cm^{-1} in infrared spectrum and at 735 cm^{-1} in Raman spectrum are assigned to these modes of vibration. The in-plane skeletal deformations, the b_{3g} (506 cm^{-1}) and the b_{2u} (618 cm^{-1}) modes in naphthalene occur without much shifting in the spectrum at 505 cm^{-1} and 607 cm^{-1} respectively. The skeletal out-of-plane deformation vibrations belong to the a'' species while the in-plane deformation vibrations belong to a' species of symmetry of the molecule.

The C-H in-plane bending modes of naphthalene are b_{1u} (810 cm^{-1}), b_{2u} (1010 cm^{-1}), a_g (1025 cm^{-1}), b_{3g} (1099 cm^{-1}), a_g (1144 cm^{-1}) and b_{2u} (1144 cm^{-1}) and the b_{3g} (1240 cm^{-1}). Though substitutions may cause small modifications in frequencies, all of these modes have been identified in IR spectrum at 830 cm^{-1} , 1010 cm^{-1} , 1023 cm^{-1} , 1038 cm^{-1} , 1100 cm^{-1} , 1150 cm^{-1} and 1245 cm^{-1} respectively. Raman frequencies at 832 cm^{-1} , 988 cm^{-1} , 1013 cm^{-1} and 1125 cm^{-1} , have been assigned to the C-H in-plane bending modes. The C-H out-of-plane bending vibrations are the 868 cm^{-1} , 878 cm^{-1} , 936 cm^{-1} and 965 cm^{-1} corresponding to the a_u (860 cm^{-1}), b_{2g} (875 cm^{-1}), b_{3g} (937 cm^{-1}) and a_u (965 cm^{-1}) modes of naphthalene respectively. No out-of-plane bending vibrations occur in the Raman spectrum of the compound. All in-plane bending modes belong to a' species and the out-of-plane bending modes to a'' species of the C_s point group of symmetry of the

molecule. The symmetrical ring breathing mode in naphthalene occurs at 760 cm^{-1} [1], but it has been assigned to the frequency at 805 cm^{-1} in IR and 802 cm^{-1} in Raman spectra of the molecule. However, it has been observed that the ring breathing mode in benzene is strongly affected by substitution. The shift in frequency is attributed to its interaction with the C–C–C in-plane bending mode, both modes belong to the same species in C_s symmetry [9,10]. The aromatic C–H stretching occur in the range $3100\text{--}3000\text{ cm}^{-1}$ [11]. In naphthalene there are two C–H stretching modes corresponding to a_g (3004 cm^{-1}) and (3055 cm^{-1}) of which a very strong absorption at 3048 cm^{-1} corresponding to C–H mode, is seen in the Raman spectra of the molecule.

Table 1. Vibrational assignment of propranolol hydrochloride.

Raman frequency (cm^{-1})	Infrared frequency (cm^{-1})	Assignment
264 (M)		C–CH ₃ bending o p
325 (W)		C–CH ₃ bending i.p.
505 (M)		Skeletal deformation i.p.
607 (S)		Skeletal deformation i p
	640 (M)	1470–830
	675 (W)	1512–830
	728 (VS)	Skeletal deformation o p.
735 (M)	738 (VS)	Skeletal deformation o p
	775 (VS)	Skeletal deformation o p
802 (M)	805 (VS)	C–C Ring breathing
832 (M)	830 (S)	C–H bending i p
	868 (M)	C–H bending o p
	878 (M)	C–H bending o p *
	908 (S)	CH ₃ Wagging
	936 (S)	C–H bending o.p.
	965 (VS)	C–H bending o.p.
988 (VS)		C–H bending i.p
1013 (S)	1010 (S)	C–H bending i.p.
	1023 (VS)	C–H bending i.p.
	1038 (VS)	C–H bending i.p.
	1080 (VS)	CH ₃ rocking
	1100 (VS)	C–H bending i.p.
1125 (M)	1150 (VS)	C–H bending i.p.
1158 (M)	1161 (S)	C–O Stretching
1188 (M)	1184 (VS)	C–N Stretching
	1220 (S)	CH ₂ rocking
	1245 (VS)	C–H bending i.p.
	1270 (VS)	C–C ring stretch

Table 1. (Cont'd.).

Raman frequency (cm ⁻¹)	Infrared frequency (cm ⁻¹)	Assignment
1287 (W)		CH ₂ twisting
	1300 (S)	2 × 1150–1010
	1329 (S)	2 × 1150–965
	1344 (S)	2 × 1184–1023
	1359 (S)	CH ₂ Wagging
	1370 (VS)	CH ₃ Symmetric bending
	1405 (VS)	CH ₂ Symmetric bending
1434 (W)		CH ₃ asymmetric bending
	1470 (VS)	CH ₃ and CH ₂ Asymmetric bending
	1512 (VS)	C–C ring stretch
	1532 (M)	C–C ring stretch
1583 (S)	1590 (VS)	C–C ring stretch
	1630 (S)	C–C ring stretch
	1650 (W)	775 + 878
	1680 (W)	738 + 936
	1741 (M)	2 × 868
	1818 (W)	805 + 1023
	1850 (W)	830 + 1023
	2080 (VW)	805 + 1270
	2115 (VW)	965 + 1150
	2145 (VW)	738 + 1405
	2402 (S)	936 + 1470
	2505 (S)	1038 + 1470
	2540 (S)	936 + 1590
2878 (M)		CH ₃ Symmetric C–H stretch
	2900 (VS)	C–H Stretchings
2928 (S)		CH ₂ Asymmetric C–H stretch
2969 (M)		CH ₃ Asymmetric C–H stretch
3048 (VS)		Aromatic C–H stretching
3295 (W)	3300 (VS)	O–H Stretching
3359 (W)		N–H Stretching

VS–Very Strong, S–Strong; M–Medium; W–Weak; VW–Very Weak, i p.–in-plane; o p.–out-of-plane.

3.2. Group vibrations :

The CH₃ symmetric and asymmetric stretching vibrations appear around a fairly constant region and they are found to occur at 2878 cm⁻¹ and 2969 cm⁻¹ respectively, in the present case [12]. The CH₂ asymmetric stretching modes appear at about 2930 cm⁻¹ and for

propranolol, it appears at 2928 cm^{-1} [13,14]. All C-H stretching vibrations appear as a very strong and broad absorption centred at about 2900 cm^{-1} in the IR spectrum. The CH_3 symmetric bending is sensitive to the atom adjacent to the CH_3 group and occurs at 1370 cm^{-1} . The CH_2 symmetric bending is placed at 1405 cm^{-1} . The CH_3 and CH_2 asymmetric deformation frequencies lie within the range and is assigned to the intense absorption at 1470 cm^{-1} [12]. In Raman spectrum, the weak absorption at 1434 cm^{-1} may be attributed to CH_3 asymmetric bending vibration. The CH_3 rocking vibration [13,15] is assigned to the 1080 cm^{-1} absorption of strong intensity. The frequency at 1220 cm^{-1} is assigned to CH_2 rocking vibration. The other group vibrations are the wagging and twisting modes. The methyl wagging is placed to 908 cm^{-1} while the CH_2 twisting occurs as a weak Raman absorption at 1287 cm^{-1} [16]. The C- CH_3 in-plane and C- CH_3 out-of-plane bending occur at 325 cm^{-1} and 264 cm^{-1} respectively.

The other vibrations for the molecule are the C-O stretching which occur at about 1159 cm^{-1} [17] and C-N stretching at about 1186 cm^{-1} [18] in both IR and Raman spectra. The N-H and O-H stretchings have been assigned to 3359 cm^{-1} and 3295 cm^{-1} respectively [19] while they give rise to a broad band of absorption in the IR spectrum of the molecule. The region between 1650 cm^{-1} and 2500 cm^{-1} is treated as due to overtones and combinations.

4. Conclusion

The infrared and Raman spectra for propranolol hydrochloride has been analysed assuming C_s point group symmetry and the observed fundamentals have been assigned to different normal modes of vibration. The assignment of the fundamental frequencies is made on the basis of magnitude and relative intensities of the observed bands. A complete vibrational assignment has been made for the molecule.

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